

The effects of confinement on rotational tunneling

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Received: 18 July 2001 / Accepted: 13 November 2001 – © Springer-Verlag 2002

Abstract. We have measured the effects of confinement on rotational tunnel splitting using neutron-backscattering spectroscopy for the molecular solid methyl iodide at low temperature. In particular, we have studied methyl iodide confined to porous glass disks with pore diameters ranging from 2.5 nm up to 20 nm. In bulk methyl iodide at low temperature, the tunnel peaks appear at $\pm 2.4 \mu\text{eV}$. In the largest pores, the tunnel peaks shift to slightly higher energy transfer and broaden. As the pore size decreases, the tunnel peaks shift to higher energy and broaden. In addition to these tunnel peaks, there is a broad spectral component, which we attribute to disordered methyl group dynamics located close to the pore walls. At the smallest confinement length scales, in pores that are 2.5 nm in diameter, there are no well-defined peaks and only this diffuse disordered spectral feature remains.

PACS: 29.30.Hs; 61.12.-q; 61.43.Gt

The extreme sensitivity of quantum rotational tunneling to the shape and magnitude of intermolecular potentials make it an ideal probe of the local molecular environment [1]. Indeed many experimental efforts have exploited this sensitivity and used rotational dynamics as a probe of disorder in mixtures of molecular solids [2] and polymers [3]. Recently rotational tunneling has been used as a probe of disorder in confined molecular solids such as H_2 [4], CH_4 [5], and CH_3I [6]. These studies have shown that the rotational dynamics can be substantially modified compared to the bulk rotational dynamics, often through the interaction with the surfaces of the confining media.

One of the challenges in studying disordered systems is understanding the origin of the differences of the rotational dynamics from that of the bulk. For a confined molecular solid identifying the specific origins of the disorder can be difficult given that there are a multitude of confining geometries available with varying confinement length scales, length scale distributions, and surface chemistry. We have begun a research program investigating the effects of pore size and

surface chemistry on the rotational dynamics of methyl iodide in porous glass disks with well-defined pore diameters and a high degree of pore interconnectedness. In this paper we present preliminary results from this investigation.

1 Methyl iodide dynamics

The dynamics of methyl iodide at low temperature, in particular those of the methyl group, can be described by a one-dimensional potential function. The simple description in the bulk can be modified to describe the rotational dynamics of confined methyl iodide [6]. In this section we provide a very brief review of bulk methyl dynamics.

At low temperature the methyl group in methyl iodide is rigid and can undergo rotations about the main (I-C) molecular axis. Thus it can be treated as a one-dimensional quantum rotor and the dynamics can be described well by a three-fold symmetric potential,

$$V(\theta) = \frac{V_3}{2}(1 - \cos 3\theta), \quad (1)$$

where θ is the angle of orientation of the methyl group and V_3 is the barrier to reorientation [7]. The Schrödinger equation for this potential can be solved numerically and the eigenvalues compared directly to the tunneling spectra. In this way one can extract the barrier height. Another layer of complexity occurs when the tunnel peaks are broadened due to disorder. In this case one may interpret the origin of the broad tunnel peak as a distribution of barrier heights arising from a distribution of local environments.

2 Experimental details

The porous glass disks used in this investigation were obtained from Geltech, Inc. [8]. Nitrogen adsorption/desorption measurements with a set of porous disks were performed in order to characterize the confinement length scales. It was found that the pore size distribution had a 10% dispersion. The disks used in these measurements had nominal pore

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diameters of 2.5, 5.8, 7.5, and 20 nm. All disks were used as-received except for one set with pore diameters of 5.8 nm which were refluxed with methanol, thus replacing the polar OH groups with methoxy groups. These disks were then dried at 150 °C for 72 hours to remove the remaining water and methanol and soaked in methyl iodide (99.4% purity) for 24 hours and sealed in an Al sample holder.

All measurements were carried out using the High Flux Backscattering Spectrometer (HFBS) [9] at the NIST Center for Neutron Research. Most measurements were performed with a dynamic range of ± 11 μeV with a corresponding instrumental resolution of 0.8 μeV .

3 Results and discussion

The results for the methyl iodide in disks with a 5.8 nm nominal pore diameter have been published elsewhere [6] and we reproduce a plot of the low-temperature data showing the model used in fitting the spectrum in Fig. 1. In addition to a small bulk-like tunneling component, there are two broad peaks located at about ± 4 μeV and a very broad diffuse component underlying the better-resolved tunnel peaks. The model used in [6] assumes a Gaussian distribution of barrier heights, V_3 . For broad distributions combined with the approximate exponential dependence of the tunneling energy on barrier height, the resulting lineshape is lognormal. For narrow distributions, the lineshape is approximately Gaussian. The bulk-like tunnel peaks can be attributed to a highly ordered molecular solid while the broad peaks at ± 4 μeV are due to a distribution of barrier heights whose mean value is lower than that in the bulk. Finally the diffuse background can be attributed to a very disordered methyl environment with a broad distribution of barrier heights. Using the tunneling data coupled with this model it

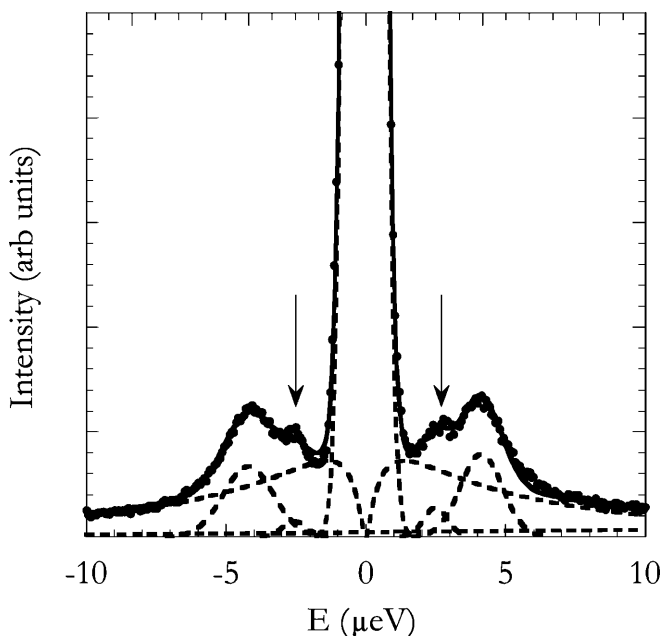


Fig. 1. Tunnel spectrum of confined CH_3I at $T = 5$ K, summed over a wavevector transfer range of 0.56 to 1.6 \AA^{-1} for 5.8 nm pores. *Dashed lines* are the fit components as described in the text and *solid line* is the entire fit. *Arrows* indicate the presence of features consistent with bulk-like tunneling

is possible to accurately predict the librational modes [6], thus lending further credibility to the model.

The existence of three separable spectral features in the data displayed in Fig. 1 suggests three environments for the methyl groups. Since CH_3I is a polar molecule and the surface of the porous glass is hydrophilic due to the presence of OH groups, it is likely that surface interactions play a significant role in the dynamics of the adsorbate. In Fig. 2 we present measurements of the spectrum at 5 K of CH_3I confined to both surface-treated and as-received porous disks. The pore filling, as determined by mass measurements and the known pore volume (from BET measurements), was determined to be $95 \pm 7\%$ full. The most prominent difference in the spectra is that the bulk-like tunneling feature has grown substantially as compared to the disordered component. Thus it appears that treatment to make the silica surface hydrophobic can substantially alter the degree of order in the adsorbed methyl iodide.

The interaction of the molecules with the surface also leads to interesting pore size dependence. Measurements of CH_3I in as-received porous disks with varying pore diameters are shown in Fig. 3. These data show that the primary tunnel peak increases in both breadth and energy transfer as the pore size decreases. The increase in breadth is an indication of an increase in the disorder of the molecular environment while the increase in the mean tunneling energy suggests a decrease in the average barrier height. We should note that a bulk-like ordered component may be present in the larger pores (7.5 nm and 20 nm) but it may be difficult to separate this from the higher energy primary peak. When the molecular solid is confined in the smallest pores, 2.5 nm, only the diffuse spectral component remains. There is a hint of a very small bulk-like component in the 2.5 nm spectrum shown in Fig. 3. However, since the overall signal was quite weak, we cannot discount the possibility that there was some CH_3I outside of the pores contaminating the signal.

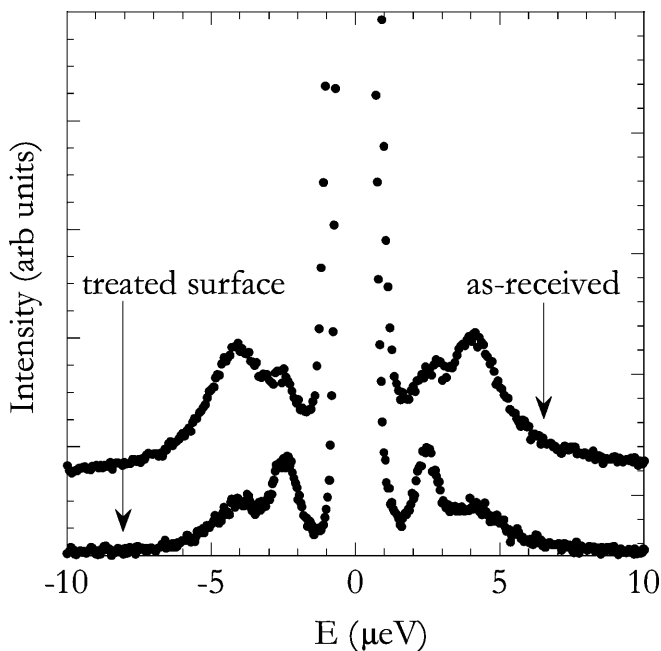


Fig. 2. Tunnel spectrum of confined CH_3I in 5.8 nm pores with and without surface treatment to make surface hydrophobic

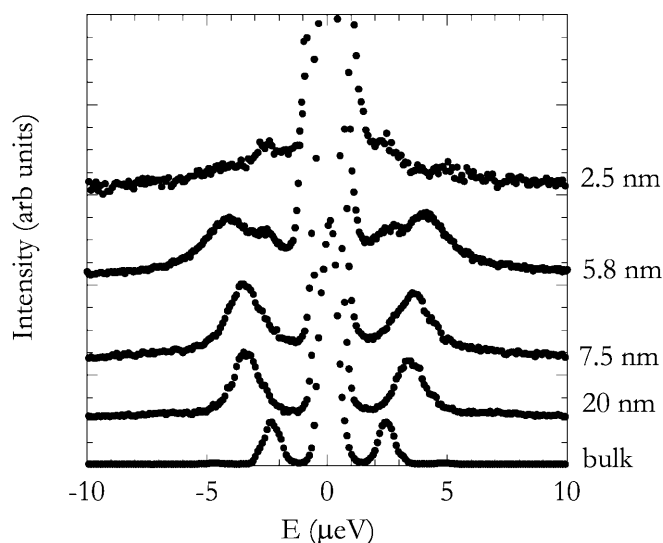


Fig. 3. Tunnel spectrum of confined CH_3I at $T = 5$ K, summed over a wavevector transfer range of 0.56 to 1.6 \AA^{-1} , for all pore sizes investigated here

4 Conclusion

We have presented preliminary results of an investigation into the effects of pore size and surface interactions on the

rotational dynamics of the molecular solid CH_3I at low temperature. Both hydrophobic and hydrophilic silica surfaces cause different methyl dynamics. Hydrophobic surfaces lead to more ordered or bulk-like response as compared to the hydrophilic. Finally we have shown that pore size can have a substantial effect on the magnitude and breadth of the methyl tunneling lineshape. A more detailed analysis of this data is in preparation [10].

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